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- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
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(54) Title: PROCESS FOR INCREASING THE SELECTIVITY OF THE HYDROGENATION OF 4,4'-DIAMINODIPHENYL-METHANE TO 4,4'-DIAMINODICYCLOHEXYLMETHANE IN THE PRESENCE OF AN N-ALKYL-4,4'-DIAMINODIPHENYLMETHANE

(57) Abstract: The invention relates to a process for increasing the selectivity of the hydrogenation of 4,4'-diaminodiphenylmethane (4,4'-MDA) to diaminodicyclohexylmethane (4,4'-HMDA) by catalytic hydrogenation of a mixture containing 4,4'-MDA as the main component and its mono-N-methyl derivative as a secondary component. According to the invention, the hydrogenation is terminated before a conversion of 4,4'-MDA to 4,4'-HMDA of 99% is achieved. Under these conditions, a substantially smaller proportion of the N-methyl-4,4'-MDA is hydrogenated to N-methyl-4,4'-HMDA.

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 392 435 A (AIR PROD & CHEM) 17 October 1990 (1990-10-17) cited in the application page 8 -page 13 ---	1
A	US 5 360 934 A (VEDAGE GAMINI A ET AL) 1 November 1994 (1994-11-01) cited in the application claims 1-19; example 1; tables 1-3 ---	1
A	EP 0 476 359 A (BAYER AG) 25 March 1992 (1992-03-25) claims 1-10; examples 1-3 ---	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 324 190 A (HUELS CHEMISCHE WERKE AG ;MOBAY CORP (US)) 19 July 1989 (1989-07-19) cited in the application abstract; claims 1-13 ---	1
A	EP 0 231 788 A (AIR PROD & CHEM) 12 August 1987 (1987-08-12) cited in the application abstract; claims 1-16; example 1; table 1 ---	1
A	EP 0 639 403 A (HUELS CHEMISCHE WERKE AG) 22 February 1995 (1995-02-22) cited in the application abstract; claims 1-9 -----	1

INTERNATIONAL SEARCH REPORT

International Application No

PC 03/06669

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0392435	A	17-10-1990	US 5026914 A	25-06-1991
			CA 2013812 A1	11-10-1990
			DE 69003570 D1	04-11-1993
			DE 69003570 T2	10-03-1994
			EP 0392435 A1	17-10-1990
			JP 2290834 A	30-11-1990
US 5360934	A	01-11-1994	BR 9402488 A	14-03-1995
			DE 69406594 D1	11-12-1997
			DE 69406594 T2	05-03-1998
			EP 0630882 A1	28-12-1994
EP 0476359	A	25-03-1992	DE 4028270 A1	12-03-1992
			CA 2050167 A1	07-03-1992
			DE 59100432 D1	04-11-1993
			EP 0476359 A1	25-03-1992
			JP 3046862 B2	29-05-2000
			JP 4247056 A	03-09-1992
			US 5245082 A	14-09-1993
EP 0324190	A	19-07-1989	AT 89260 T	15-05-1993
			CA 1331200 C	02-08-1994
			DE 3881012 D1	17-06-1993
			DE 3881012 T2	14-10-1993
			EP 0324190 A2	19-07-1989
			JP 2000738 A	05-01-1990
			JP 2675116 B2	12-11-1997
			US 5196594 A	23-03-1993
EP 0231788	A	12-08-1987	US 4754070 A	28-06-1988
			CA 1271491 A1	10-07-1990
			DE 3762616 D1	13-06-1990
			EP 0231788 A1	12-08-1987
			JP 1012745 B	02-03-1989
			JP 1526542 C	30-10-1989
			JP 62228044 A	06-10-1987
			US 4946998 A	07-08-1990
EP 0639403	A	22-02-1995	DE 4328007 A1	23-02-1995
			DE 59403525 D1	04-09-1997
			EP 0639403 A2	22-02-1995
			ES 2106415 T3	01-11-1997
			JP 7080305 A	28-03-1995
			US 5578546 A	26-11-1996
			ZA 9406297 A	23-03-1995